A Study of Pyridinium-Type Functional Polymers. I. Preparation and Characterization of Soluble Pyridinium-Type Functional Polymers

GUANGJI LI,* JIARUI SHEN, and YINLAN ZHU

Department of Polymer Science and Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China

SYNOPSIS

Copolymerization of 4-vinylpyridine (4VP) with styrene (St) was performed in ethanol using 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and then a random copolymer P(4VP–St) was obtained. A soluble pyridinium-type polymer containing N-benzyl-4-vinylpyridinium bromide [Q-P(4VP–St)], was prepared by quaternization of P(4VP–St) with benzyl bromide (BzBr). The structures of P(4VP–St) and its quaternized product Q-P(4VP–St) were identified by FTIR. The 4VP content in P(4VP–St) and the pyridinium group content (C_q) in Q-P(4VP–St) were determined by nonaqueous titration and argentometry, respectively. The molecular weight of p(4VP–St) was characterized by intrinsic viscosity. In addition, the charge density σ of the soluble pyridinium-type polymers was measured by colloid titration, and the mathematical relation between σ and C_q was established as follows: $\sigma = -0.090 + 0.942 \, C_q$. A preliminary investigation was made into the viscosity behavior and electroconductivity of the Q-P(4VP–St)/polar solvent system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Pyridinium-type polymers have been found to possess unique properties in the coagulation of microbial cells, capture or isolation of bacteria and viruses, water disinfection, and removal organic pollutants from the aquatic environment. As a new type of functional polymer material, they are expected to be used as an immobilized biocatalyst carrier, a sensitive material used in a biosensor, a reagent for water treatment, and so forth. Therefore, pyridinium-type polymers have attracted increasing attention of researchers for many years.

In this research field, Japanese professor Kawabata and co-workers successively reported the properties of soluble and insoluble pyridinium-type polymers in killing bacteria,[1] coagulating and sedimentating microbial cells,[2] capturing bacteria and viruses,[3–8] and removing organic pollutants from the aquatic environment.[9–12] The studies revealed their broad prospects for development and application in the fields of bioengineering, bioinstrumentation, and environmental protection. In this work, the preparation and characterization of soluble pyridinium-type polymers are discussed.

EXPERIMENTAL

Materials

Comonomers 4-vinylpyridine (4VP) and styrene (St) were purified by distillation under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was refined by recrystallization twice. Other chemicals and solvents were used without further purification.

Preparation of Samples

Both the synthesis and the quaternization of the copolymer P(4VP–St) of 4VP with St were carried out in a four-necked round-bottom flask equipped

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with a thermometer, a mechanical stirrer, a nitrogen inlet, and a reflux condenser. Copolymers P(4VP–St) of varying compositions were synthesized by the solution polymerization of comonomers 4VP and St having a prescribed ratio using AIBN as an initiator in ethanol at 75–80°C for 6 h under a nitrogen atmosphere. P(4VP–St) was isolated by pouring the reaction mixture into petroleum ether, washed with distilled water, and dried *in vacuo* to a constant weight.

The thus-obtained P(4VP–St) was dissolved in ethanol and quaternized with an excess of benzyl bromide (BzBr) at 75–80°C under a nitrogen atmosphere. After 6 h, the product was reprecipitated with petroleum ether and dried *in vacuo*. Thus, the soluble pyridinium-type polymer in the bromide form, Q-P(4VP–St), was obtained. To thoroughly remove oligomers and other impurities in it, Q-P(4VP–St) was purified by Soxhlet extraction using petroleum ether as an extractant for 24 h.

Polymer Characterization

Nonaqueous Titration

The 4VP content in P(4VP–St) was determined according to a procedure previously developed by Burleigh et al.[13] with minor modifications.

Intrinsic Viscosity

Benzene and ethanol were used as the solvents of P(4VP–St) with low and high 4VP contents, respectively. The intrinsic viscosity $[\eta]$ of P(4VP–St) was measured using a Ubbelohde viscometer in a thermostat at 25 ± 0.5°C. $[\eta]$ indirectly reflects the molecular weight of P(4VP–St).

Argentometry

The pyridinium group content (i.e., the content of the quaternized 4VP ring) in each soluble pyridinium-type polymer, C_q, was determined by argentometry using ferric ammonium sulfate as an indicator.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of P(4VP–St) and Q-P(4VP–St) were recorded in KBr pellets using an Analect RFX-65 spectrophotometer.

Colloid Titration

The colloid titration method was used to measure the charge density of Q-P(4VP–St), σ. The dilute

solution of Q-P(4VP–St) containing 2–3 drops of 0.1% toluidine blue (TB) solution as an indicator was titrated with the standard solution of potassium polyvinylsulfate (KPVS). The end point in the titration can be determined by the color change of TB from blue to red-purple.

Solution Behavior

The solution of Q-P(4VP–St) was prepared by dissolving the *vacuo*-dried Q-P(4VP–St) sample in the polar solvent dimethylformamide (DMF). The viscosity of the Q-P(4VP–St)/DMF solution system was measured using a Ubbelohde viscometer in a thermostat at 30 ± 0.5°C. The specific conductivity of the system, κ, was measured using a DDS-11A conductometer (made in the Shanghai No. 2 Analysis Instrument Factory) at room temperature.

RESULTS AND DISCUSSION

Synthesis of P(4VP–St)

P(4VP–St) is a precursor copolymer used to prepare a soluble pyridinium-type polymer Q-P(4VP–St). To make Q-P(4VP–St) become a water-soluble polymer containing both hydrophobic St chain units and hydrophilic pyridinium groups, it must be avoided to produce long St blocks in the P(4VP–St) backbone besides controlling the ratio of comonomers in the synthesis of P(4VP–St).

By adjusting the mol fraction of 4VP in the feed, f_1, between 0.1 and 1.0, a series of P(4VP–St) copolymers having different compositions were synthesized. Conversion by weight for the copolymerization, C_w, was calculated after drying the product to constant weight. The data on f_1 and C_w for the copolymerization are listed in Table I. From the results of nonaqueous titration, the mol fraction in each P(4VP–St) sample, F_1, was calculated. The plot of F_1 vs. f_1 for the copolymerization is shown in Figure 1.

It can be seen from Table I that the conversion C_w increases with an increasing mol fraction of 4VP in the feed, f_1. When $f_1 \geq 0.6$, C_w can reach greater than 85%. It shows that 4VP is more active than is St. In addition, the plot in Figure 1 directly reflects the relation between the copolymer composition and the feed composition for the copolymerization of 4VP with St. In the copolymer samples A1–A6, $f_1 < 0.7$, then $F_1 > f_1$; in sample A7, $f_1 = 0.7$, then F_1 is close to f_1; and in sample A8, $f_1 > 0.7$, then $F_1 < f_1$. This result indicates that the copolymerization of 4VP with St is a nonideal copolymerization with a

Table I Relation Between C_w and f_1 for the Copolymerization of 4VP with St

Copolymer No.	f_1	C_w (wt %)
A1	0.1	55.73
A2	0.2	64.78
A3	0.3	64.57
A4	0.4	68.39
A5	0.5	71.00
A6	0.6	86.20
A7	0.7	85.94
A8	0.8	90.55
A9	1.0	93.33

constant ratio point and the reactivity ratios of 4VP and St should be less than 1. In the case of high conversion C_w, the constant ratio point $(f_1)_{constant}$ is about 0.695. When $f_1 < 0.695$, $F_1 > f_1$ and vice versa. This reaction characteristic is in accord with the data on the reactivity ratio, r_1(4VP) = 0.7 ± 0.1 and r_2(St) = 0.54 ± 0.03, reported in the literature.[14]

Identification of P(4VP–St) and Its Quaternized Product

A series of double pyridinium-type polymers, Q-A1, Q-A2, . . . , Q-A9, were obtained by quaternizing the copolymers A1, A2, . . . , A9, respectively. FTIR was used to identify the prepared P(4VP–St) and Q-P(4VP–St). A representative example is presented in Figure 2, where the spectra of the P(4VP–St) sample A6 and its quaternized product Q-A6 are presented together with that of PSt (the homopolymer of St). The spectrum of A6 exhibits the characteristic absorption peaks of 4VP located at 1414 and 817 cm^{-1}, which are, respectively, attributable to the symmetric C — N stretching vibration[15-17] and the C — H out-of-plane bending vibration[17,18] of the pyridine ring in 4VP chain units and those of St located at 906 and 757 cm^{-1}.[18] This suggests that the sample A6 contains both the chain units of 4VP and St. In the spectrum of Q-A6, a peak at 1414 cm^{-1} disappeared and a new peak at 1630 cm^{-1}, assigned to the absorbance of quaternized pyridine ring,[19] appeared. This result proves that the 4VP chain units in Q-A6 had been completely quaternized.[15,16]

According to its characteristics, the copolymerization of 4VP with St is random and the resultant P(4VP–St) should be a random copolymer. On the other hand, in the light of fact that PSt is not dissolved in polar solvents like ethanol, glacial acetic acid, and dimethylformamide and that P(4VP–St)
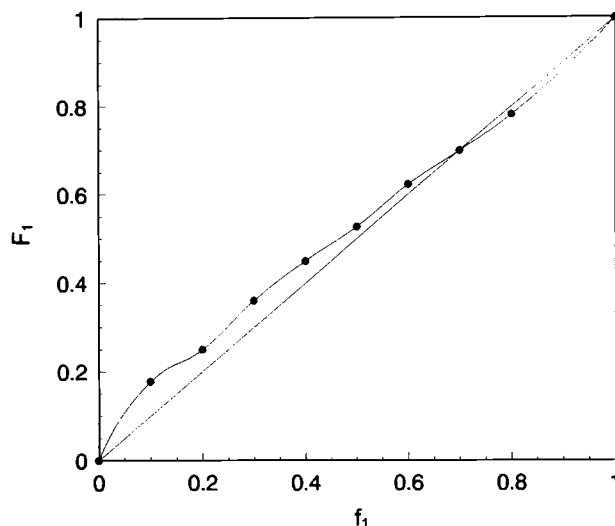
Figure 1 Copolymer composition as a function of feed composition for the copolymerization of 4VP with St. The straight line represents ideal random copolymerization.

is dissolved in these solvents, the possibility of containing the homopolymer of St and the long St blocks in P(4VP–St) can be excluded. The above analyses fully testify that P(4VP–St) samples synthesized in our experiment are random copolymers and the quaternization of these polymer is successful, so the aim of preparing soluble pyridinium-type polymers is achieved.

Figure 2 FTIR spectra of PSt, A6, and Q-A6.

Table II The Intrinsic Viscosity [η] of P(4VP–St) Samples

Copolymer No.	Solvent	[η] (dL/g)	Copolymer No.	Solvent	[η] (dL/g)
A1		0.175	A5		0.198
A2		0.105	A6		0.171
A3	Benzene	0.174	A7	Ethanol	0.308
A4		0.088	A8		0.236
—	—	—	A9		0.230

Characterization of Soluble Pyridinium-type Polymers
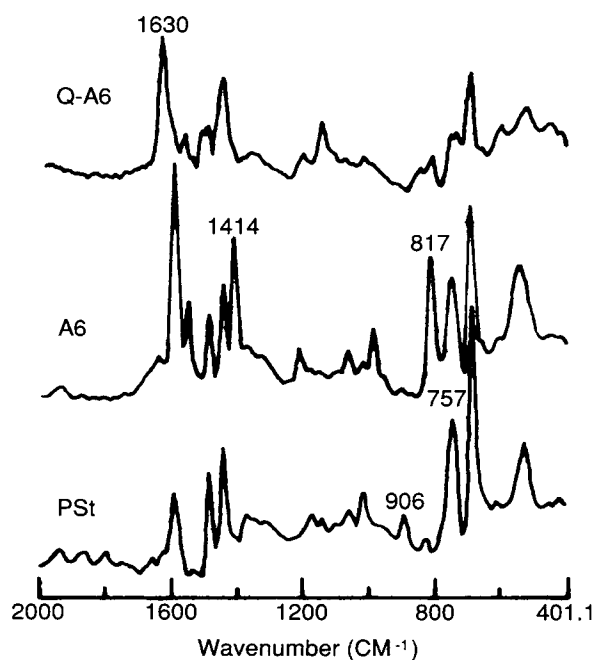
Intrinsic Viscosity [η]

The molecular weight of an ionic polymer may be characterized by that of its precursor polymer. Thus, the relation between viscosity and concentration of solutions of copolymers with various compositions was measured respectively and the intrinsic viscosity [η] was calculated to indirectly characterize the molecular weights of the corresponding soluble pyridinium-type polymer. The results are compiled in Table II.

Composition Analysis of Polymers

Seeing that a titration of the polymer solution was likely to be affected by macromolecular conformation in medium so that the titrating reaction could not be completed instantaneously, the manner of back titration in argentometry was selected to determine the pyridinium group content in each Q-P(4VP–St) sample, C_q. From C_q and the mol fraction of 4VP in the corresponding precursor copolymer, the degree of quaternization (DQ) and the ion content (C_{ion}) of Q-P(4VP–St) were calculated. The analysis results are presented in Table III. In the meantime, the elemental analysis of a representative

Table III Composition Analysis of the Soluble Pyridinium-type Polymers

Sample No.	C_q (mmol/g)	DQ (%)	C_{ion} (mol %)
Q-A1	1.106	80.11	14.22
Q-A2	1.689	99.31	24.79
Q-A3	2.153	98.86	35.62
Q-A4	2.478	99.36	44.69
Q-A5	2.699	99.54	52.49
Q-A6	2.921	98.21	61.14
Q-A7	3.094	98.52	68.88
Q-A8	3.237	97.40	76.09
Q-A9	3.375	83.96	83.96

sample Q-A6 was carried out using Heraeus elemental analyzer to examine the reliability of argentometry. Table IV lists the data obtained by elemental analysis.

In Table III, the DQ values of all samples, excepting Q-A1 and Q-A9 with the lowest and the highest 4VP content, respectively, are close to 100%. By making a comparison between the composition analysis results of Q-A6 listed in Table III and those in Table IV, it is seen that the results obtained by use of both argentometry and elemental analysis are basically in concordance. Moreover, the disappearance of the pyridine band at 1414 cm^{-1} for 4VP in the FTIR spectrum of Q-A6 (as shown in Fig. 2) can be taken as evidence of complete quaternization.[15,16] Therefore, the data on composition analyses obtained by argentometry in Table III are reliable.

Charge Density (σ)

As a nitrogen-containing cationic polymer, a soluble pyridinium-type polymer will inevitably display many features pertaining to an ionic polymer. Considering the prepared soluble pyridinium-type polymers, their ion contents (see Table III) almost exceed the range of ion content in conventional ionomers (<10–15 mol %),[20,21] and then the charge density on their macromolecular chains is greater than that of a conventional ionomer, but lower than that of polyelectrolytes, which contain almost one charge per monomer.[21] A change in the charge density σ of the soluble pyridinium-type polymers will undoubtedly influence their properties, especially the interaction between the polymers and bacterial cells bearing a negative

Table IV Elemental Analysis Result of Q-A6

N (%)	Br (%)	C_q (mmol/g)	DQ (%)	C_{ion} (mol %)
3.90	22.12	2.768	99.35	55.07

Table V   The Data on Charge Density of Soluble Pyridinium-type Polymers

Sample No.	σ (meq/g)	Sample No.	σ (meq/g)
Q-A1	1.051	Q-A6	2.630
Q-A2	1.418	Q-A7	2.780
Q-A3	1.908	Q-A8	2.944
Q-A4	2.243	Q-A9	3.224
Q-A5	2.432	—	—

charge. For this reason, the charge density of each soluble pyridinium-type polymer was measured by colloid titration.

Because it is a cationic polymer, the soluble pyridinium-type polymer can be directly titrated with standard polyanion potassium polyvinylsulfate (KPVS) in solution. The polymer reacts with KPVS to produce the sediment of polyelectrolyte complex. The reaction is expressed as follows:

The data on charge density σ (meq/g) calculated from colloid titration results are presented in Table V.

By comparing the σ value of each sample in Table V with the corresponding C_q value in Table III, it is found that σ increases with increase in C_q. This is because the charges of the soluble pyridinium-type polymer come from the dissociation of its pyridinium groups. The relationship between σ and C_q was analyzed using linear regression. As a result, the mathematical equation reflecting this relationship was established as follows: $\sigma = -0.090 + 0.942\, C_q$, and the linear correlative coefficient was 0.995. This proves that the σ values obtained by colloid titration is in good agreement with those obtained by argentometry for the soluble pyridinium-type polymers whose content of pyridinium groups is between 1.11 and 3.38 mmol/g, i.e., the quantity of σ essentially reflects that of C_q.

Viscosity Behavior of Q-P(4VP–St)/DMF Solution System

The soluble pyridinium-type polymers can be easily dissolved in polar solvents with a high dielectric constant. In such solution systems, substantial changes in the number and state of counterions bound on the polymer chain may occur along with the difference of the ion contents or charge densities and the polymer concentrations, so as to modify the polymer conformation and then to proceed to its solution properties. These changes were investigated by measuring the relation between the reduced viscosity (η_{sp}/c) and polymer concentration (c) for each Q-P(4VP–St)/DMF and the corresponding P(4VP–St)/DMF systems. As shown in Figures 3–5, the plots of η_{sp}/c vs. c reveal the effect of the ion content and concentration of Q-P(4VP–St) on the viscosity behavior of the Q-P(4VP–St)/DMF system.

It is very obvious that the viscosity behavior of the unquaternized copolymers (A1–A9) in DMF is identical with that of a common polymer. Their plots of η_{sp}/c vs. c are straight lines and the η_{sp}/c values are lower than those of the corresponding Q-P(4VP–St)/DMF systems. The reduced viscosity η_{sp}/c of all Q-P(4VP–St)/DMF systems increases remarkably with decreasing polymer concentration c, showing a typical polyelectrolyte behavior or effect.

In general, ion-containing organic macromolecules without crosslinks may be classified as two types of polymers depending on the charge densities[21]: the ionomers and the polyelectrolytes. The former is a class of ion-containing polymers,

Figure 3   Reduced viscosity (η_{sp}/c) as a function of polymer concentration (c) for Q-P(4VP–St) (Q-A1–Q-A4) of various ion contents and the corresponding P(4VP–St) in DMF.
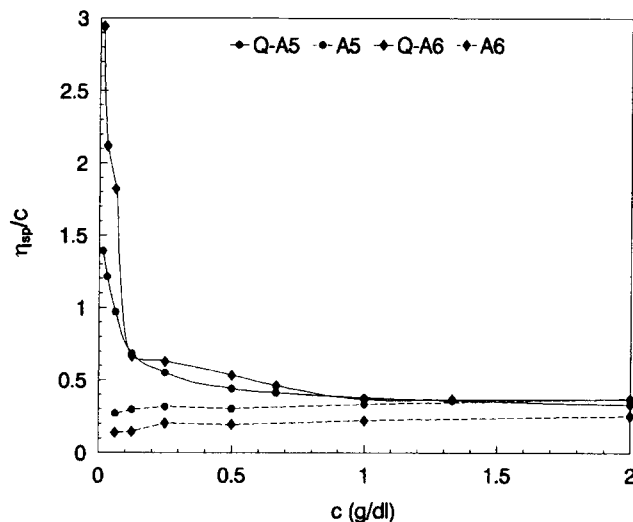
Figure 4 Reduced viscosity (η_{sp}/c) as a function of polymer concentration (c) for Q-P(4VP–St) (Q-A5, Q-A6) of various ion contents and the corresponding P(4VP–St) in DMF.

which have ionic groups in concentration up to 10–15 mol%, distributed in nonionic backbone chains,[20,22,23] while the latter is usually homopolymer containing almost one charge per monomer.[21] In the prepared soluble pyridinium-type polymers, Q-A1 may be considered as an ionomer since its C_{ion} is somewhat lower than 15 mol %; Q-A9 may be considered as a polyelectrolyte since it has the highest C_{ion} (83.96 mol %) and its backbone chains are the homopolymer of 4VP; and Q-A2, Q-A3, . . . , Q-A8, whose ion contents are much higher than 15 mol % and whose backbone chains are the copolymer of 4VP with St, cannot be considered as either ionomers or polyelectrolytes according to the above definitions. However, they possess some properties in common with ionomers and polyelectrolytes. Ionomers in polar solvents can also exhibit the typical polyelectrolyte behavior.

In the ionomer/polar solvent system with very low polymer concentration, it has been conformed that η_{sp}/c increases with increase in the ion content, and from low-angle light scattering measurements, the effective diameter of macroions (fixed ions) is directly proportional to the ion content.[24] The effective diameter reflects the range of intermolecular repulsive interactions.[24] Because the intrinsic viscosities of A1, A2, and A5 are, respectively, close to those of A3, A4, and A6, the molecular weights of Q-A1, Q-A2, and Q-A5 approximate those of Q-A3, Q-A4, and Q-A6, respectively. In Figures 3 and 4, by comparing the polyelectrolyte behavior for Q-A1/DMF, Q-A2/DMF, and Q-A5/DMF systems with

that for the corresponding solution systems of Q-A3, Q-A4, and Q-A6, respectively, it can be observed that the polyelectrolyte behavior is enhanced with increase of the ion content. But such a regular change is not observed in Figure 5. Conversely, Q-A7, Q-A8, and Q-A9 with a high ion content in DMF show weaker polyelectrolyte behavior than that of the samples with low ion content. This experimental result cannot be interpreted by means of the theory concerning the solution behavior of the ionomer/polar solvent system.

Since the increase in the reduced viscosity of the ionic polymer/polar solvent system with dilution is always attributed to a polyelectrolyte effect,[21] the solvation mechanism for a soluble pyridinium-type polymer in polar solvent is analogous to that for polyelectrolytes in aqueous solutions, i.e., the polymer macromolecules in polar solvents can be dissociated into macroions and small ions or counterions. With dilution, the number of counterions diffusing into the pure solvent domain increases, the screening effect of counterions becomes weaker, the net charges on macroions increase, and then the repulsions between fixed ions on the polymer chain also increase, leading to a full extension of the polymer chain and, consequently, to a remarkable increase of the reduced viscosity.[25] As for the soluble pyridinium-type polymers with a relatively small difference in molecular weights, the higher the ionic group content is, the more the ionic groups per polymer chain are. Thus, according to the above-men-
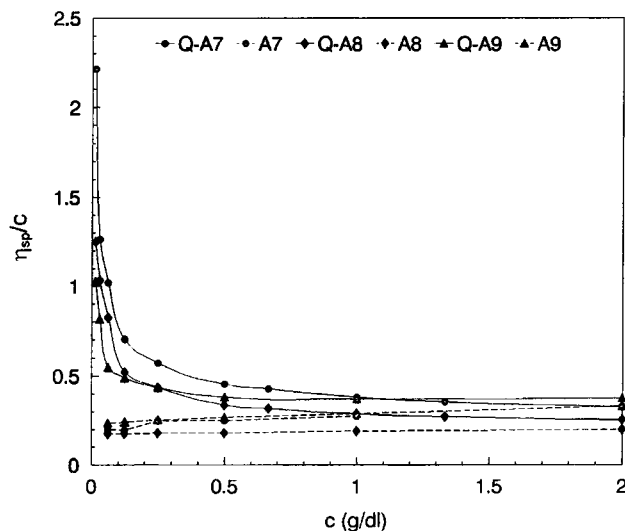

Figure 5 Reduced viscosity (η_{sp}/c) as a function of polymer concentration (c) for Q-P(4VP–St) (Q-A7, Q-A8, Q-A9) of various ion contents and the corresponding P(4VP–St) in DMF.

tioned theory, the intramolecular electrostatic repulsions are strengthened as a result of an increase in the number of ionic groups per polymer chain so that the polymer chains in the solution can extend more fully and the polyelectrolyte behavior of the solution becomes more remarkable with an increase in ion content. The η_{sp}/c vs. c plots of Q-P(4VP–St)/DMF systems as shown in Figures 3 and 4 are accordant with this principle. As for the experimental phenomenon in Figure 5 that the soluble pyridinium-type polymers with high ion content in DMF display a relatively weak polyelectrolyte effect, it may be explained by the theory of counterion condensation proposed by Manning.[26]

In a polyelectrolyte/water solution, macroions can bind the surrounding counterions to a certain extent. The binding ability is related to the charge density of macroions. According to the theory of counterion condensation, if the linear charge density exceeds a critical value, the solution system is theoretically unreasonable and actually unstable. A fraction of the counterions will "condense" on the macroion to neutralize part of the linear charges, so as to reduce the effective charge density to this critical value and finally to make the system stable.[21,26,27] For this reason, the distance between macroions and counterions in the Q-P(4VP–St)/DMF solution will decrease due to a high charge density of Q-P(4VP–St) and the screening effect of the counterions will increase. As a result, the net charge on the macroions decreases, the extension of the polymer chain is suppressed, and the polyelectrolyte effect of solution is weakened. Therefore, it is possible for the counterion condensation to occur in the solution systems of Q-A7, Q-A8, and Q-A9 with a high charge density in DMF, thus causing the solution system to exhibit a relatively weak polyelectrolyte behavior.

The above-mentioned analyses indicate that although the structure of Q-P(4VP–St) differs from that of a traditional polyelectrolyte, the viscosity behavior of the Q-P(4VP–St)/DMF solution system possesses the characteristics of the polyelectrolyte solution, and the effects of ion content or charge density of Q-P(4VP–St) on the viscosity behavior of the system can be explained by the theory concerning the polyelectrolyte solution. On the other hand, the effect of the ion content on the viscosity behavior of the system is different from the conventional ionomer/polar solvent system although their viscosity behaviors have some properties in common. Therefore, it is more reasonable to take the soluble pyridinium-type polymers possessing a high ion content and containing hydrophobic chain units as polyelectrolytes.

In 1990, Eisenberg and Rinaudo[28] proposed new definitions for ionomers and polyelectrolytes no longer based on charge densities but on their behavior. Ionomers can be defined as "polymers in which the bulk properties are governed by ionic interactions in discrete regions of the material (the ionic aggregates)" and polyelectrolytes as "polymers in which solution properties in solvents of high dielectric constants are governed by electrostatic interactions over distances larger than typical molecular dimentions." Hence, a polymer containing a few percent of an ionic group dissolved in a polar solvent should be considered as a polyelectrolyte. In fact, these definitions are already accepted. An ionomer dissolved in polar solvent was already often called a weakly charged polyelectrolyte.[21] According to the new definitions of ionomers and polyelectrolytes, the prepared soluble pyridinium-type polymers are undoubtedly a new type of cationic polyelectrolyte containing hydrophilic ionic groups and hydrophobic chain units.

Specific Conductivity (κ) and Equivalent Conductance (Λ) of Q-P(4VP–St)/DMF Solution System

Under the action of a solvent, the macroions and counterions of the Q-P(4VP–St) dissolved in a polar solvent can exist in a variety of conformations because of changes in the interactions between them and between the ions and the solvent. This will have an effect upon not only the viscosity behavior of the system, but also on its conductive property. To further investigate the solution behavior of soluble pyridinium-type polymers, the specific conductivity κ of the Q-P(4VP–St)/DMF system, in which the initial polymer concentration c_0 was 2.0 g/dL, was measured in the case of gradual dilution. From the C_q of the sample and the concentration and κ of its solution, the normal concentration of pyridinium groups in the solution was first calculated and then the equivalent conductance Λ was figured out. Λ represents the conductive ability of the Q-P(4VP–St)/DMF solution containing 1 equivalent of ionic groups. Table VI presents the data on κ and Λ of each Q-P(4VP–St)/DMF system.

In Table VI, it is seen that as the polymer concentration decreases in the given Q-P(4VP–St)/DMF system κ decreases and Λ increases. This is analogous to the conductive property of a small molecular electrolyte in a solution,[29] but the reasons for this are much more complicated: When the polymer concentration decreases, the total ion concentration in the solution system also reduces, leading

Table VI   The Data on Conductive Property of Each Q-P(4VP–St)/DMF System

Sample No.	c_0		$(\frac{2}{3})c_0$		$(\frac{1}{2})c_0$		$(\frac{1}{3})c_0$		$(\frac{1}{4})c_0$	
	κ (s/m)	$\Lambda \times 10^3$ (s m²/eq)	κ (s/m)	$\Lambda \times 10^3$ (s m²/eq)	κ (s/m)	$\Lambda \times 10^3$ (s m²/eq)	κ (s/m)	$\Lambda \times 10^3$ (s m²/eq)	κ (s/m)	$\Lambda \times 10^3$ (s m²/eq)
Q-A1	0.0499	2.248	0.0369	2.493	0.0286	2.576	0.0220	2.973	0.0178	3.207
Q-A2	0.0575	1.701	0.0419	1.859	0.0320	1.893	0.0246	2.183	0.0200	2.367
Q-A3	0.0655	1.523	0.0482	1.681	0.0400	1.860	0.0294	2.051	0.0234	2.176
Q-A4	0.0602	1.214	0.0436	1.318	0.0350	1.411	0.0249	1.506	0.0200	1.613
Q-A5	0.0508	0.941	0.0375	1.042	0.0304	1.126	0.0220	1.222	0.0180	1.333
Q-A6	0.0574	0.983	0.0421	1.081	0.0350	1.199	0.0255	1.310	0.0204	1.397
Q-A7	0.0448	0.790	0.0366	0.888	0.0288	0.932	0.0206	1.000	0.0154	0.997
Q-A8	0.0415	0.640	0.0324	0.750	0.0260	0.802	0.0199	0.921	0.0164	1.012

to a decrease in κ, and, on the other hand, the resistance to the counterion transport decreases, leading to increases in the transport rate and the mobility of counterions and, consequently, to an increase in κ. In this experiment, the factor causing the specific conductivity κ to decrease seems to play a dominant role. Actually, many factors such as the solution viscosity, the polymer chain conformation, and the interactions between polymer and solvent all directly or indirectly modify the conductive property of the solution system. The case concerning an increase in Λ with decreasing polymer concentration shows that the same number of ionic groups can have a greater contribution to the electroconductance of the system in a state of the diluted solution than in a state of the undiluted solution.

The data in Table VI still indicate that in the Q-P(4VP–St)/DMF systems with equal polymer concentration κ increases with increasing C_q if the used polymers are Q-A1, Q-A2, and Q-A3 with a low C_q. This is obviously because the higher is the C_q of the polymer the higher is the actual ion concentration in its solution system. However, if the used polymers are Q-A4, Q-A5, ..., Q-A8 in the systems, κ does not increase with rising C_q of the polymer, but decreases. In other words, an extreme value of κ appears when the C_q of Q-P(4VP–St) in the solution system is about 2.2 mmol/g (the pyridinium group content of Q-A3). Within the concentration range of the Q-P(4VP–St)/DMF solution measured, the κ of Q-A8 with the highest C_q in DMF is almost the lowest. The reason for this may be that the macroions in the solution composed of DMF and Q-P(4VP–St) with a high C_q value often possess a high charge density so as to produce a strong overlapping electric field, which will greatly limit the activities of counterions, making their transport rate and mo-bility decrease and, consequently, reducing the specific conductivity κ of the solution.

It is worth noticing that the equivalent conductance of Q-P(4VP–St)/DMF systems, Λ, almost decreases with an increase in the C_q of the polymer. It implies that the distributional density of an equal number of ionic groups along the polymer chain can have an effect on the conductive property of the system. It is clear that ionic groups tend to be densely bound on the macromolecular chain for the polymer with a high C_q. So, in its solution, the macroions can produce a relatively strong overlapping electric field so as to strengthen the ability of binding counterions and to reduce the counterion mobility. As a result, the equivalent conductance of the solution, Λ, decreases. But in the solution of the polymer with a low C_q, the case is exactly the reverse.

Since the activity of cations chemically bound on a polymer chain is negligible as compared with counterions,[30] only the contributions of counterions to the conductive property of Q-P(4VP–St)/DMF systems is considered in the above analyses. In brief, besides the inherent properties of a soluble pyridinium-type polymer and solvent DMF, the interaction between polymer and solvent, the viscosity of solution, the polymer conformation, the interactions between macroions and counterions, the repulsion among polymer chains, and so on will all influence the dissociation of pyridinium groups and the counterion transport, thus modifying the conductive property of Q-P(4VP–St)/DMF systems. To clarify these effects, there is much research work to do.

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